JOURNAL OF CATALYSIS **143**, 533–538 (1993)

Methane Coupling Reaction on Oxide Solid Solution Catalysts[1]

C. B. ALCOCK,* J. J. CARBERRY,† R. DOSHI,* AND N. GUNASEKARAN†

*Center for Sensor Materials, Department of Electrical Engineering, and †Laboratory for Catalysis, Department of Chemical Engineering, University of Notre Dame, Notre Dame, Indiana 46556

Received January 25, 1993; revised May 10, 1993

The methane coupling reaction to form C_2 hydrocarbons has been studied over perovskite-type oxides $La_{1-x}Sr_xB_{1-y}M_yO_{3-\delta}$($B$ = Co, Cr, Fe, Mn, Y; M = Nb, Ti), K_2NiF_4-type superconducting oxides $A_{2-x}B_xCuO_{4-\delta}$(A = La, Nd; B = Sr, Ce), and the solid solution $La_{0.9}Sr_{0.1}O_{1.45}$. The reaction was performed in a fixed bed flow reactor with a feed containing 30% methane, 5% oxygen, and balance helium at 795°C. The results indicated that the superconducting oxides and the perovskites with high p-type electronic conductivity were not active for the methane conversion to C_2 hydrocarbons. The compounds with n-type conductivity, electrolytes, and insulators were all found to proceed with selective oxidation to C_2 compounds. A combination of an insulator or electrolyte associated with increased oxygen vacancy concentration appears to increase the C_2 yield. Electrical conductivity, oxygen diffusion coefficient, and oxygen vacancy concentrations of the materials were considered to explain the observed variations in the methane coupling reactivity. © 1993 Academic Press, Inc.

INTRODUCTION

Perovskite oxides of the formula ABO_3 (A = La, Sr; B = Cr) and other oxides of the general formula A_2BO_4 (A = La, Sr; B = Cu) have been shown to be catalytically active for CO oxidation (*1*–*3*). All the oxides of the type $La_{1-x}Sr_xBO_{3-\delta}$ (B = Cr, Co, Fe, Mn) are good electronic conductors (*4*–*7*). The mode of electrical conduction of these oxides and of the $La_{2-x}Sr_xCuO_{4-\delta}$ system is p-type. It has recently been shown that the n-type superconducting oxide system, $Nd_{2-x}Ce_xCuO_{4-\delta}$ (*8*), is less active for CO oxidation than the p-type conductors, and the perovskite electrolyte, $La_{0.8}Sr_{0.2}YO_{3-\delta}$ (*8*), is catalytically inactive in this regard. Other studies on the oxidation of hydrocarbons (*9*, *10*) indicate that the perovskite oxide catalysts are comparable in their activity to Pt/alumina catalysts. While some metal oxides such as NiO and MnO_2 are known to be active catalysts for hydrocarbon oxidation, it has been shown that combinations of metal oxides can be better catalysts than the component oxides (*11*). Catalytic oxidation is an important property for the oxidation of undesirable components in exhaust gases, whereas oxidative coupling of methane to produce higher hydrocarbons is important in the use of the abundant quantities of methane available in natural gas, and so both aspects of catalysis are important.

The oxidative coupling of methane has been observed for several oxide catalyst systems (*12*, *13*) and efforts have been made to increase the activity by "promoting" the oxides with other metals such as Li on MgO. Many of these efforts have been made on materials of which the structure has not been well characterized from the crystallographic point of view.

In this study we measured the catalytic properties of well characterized bulk solids whose structure, stability, and electrical properties are well known. Perovskite oxides of the general formula $La_{1-x}Sr_x B_{1-y}O_{3-\delta}$ (B = Co, Cr, Fe, Mn, Y; M = Nb, Ti), oxides in the superconducting systems

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[1] Presented at the Symposium on Natural Gas Upgrading, ACS Meeting, April, 1992.

0021-9517/93 $5.00

$A_{2-x}B_xCuO_{4-\delta}$ (A = La, Nd; B = Sr, Ce), and oxides in the La–Sr–Y–O system were examined for oxidative coupling of methane and the results compared with the known defect and electronic properties of these oxides. The compounds included in this study encompass a wide range of electrical properties from superconducting oxides ($La_{2-x}Sr_xCuO_{4-\delta}$, $Nd_{2-x}Ce_xCuO_{4-\delta}$), highly semiconducting p-type oxides ($La_{0.8}Sr_{0.2}BO_{3-\delta}$; B = Co, Cr, Mn), an n-type semiconductor ($LaFe_{0.8}Nb_{0.2}O_{3-\delta}$), and a purely ionic conductor ($La_{0.8}Sr_{0.2}YO_{2.9}$), to insulators (La_2O_3, $LaYO_3$, Y_2O_3, and SrO). This study is not an optimized performance evaluation of catalysts but an attempt to evaluate the characteristics of catalytic activity in relation to the well known bulk properties of the catalysts.

EXPERIMENTAL

(*i*) *Preparation of Oxides by Solid-State Processing*

All the oxides except $LaYO_3$-bixbyite and $La_{0.9}Sr_{0.1}O_{1.45}$ were prepared by the classical solid-state processing method. The component oxides were mixed in the proper proportions, pressed into pellets of 1 cm diameter under a load of 20,000 lbs and sintered at 1100°C. The pellets were then crushed and ground, and the process was repeated several times until a single-phase material was obtained.

$LaYO_3$ and $La_{0.8}Sr_{0.2}YO_{3-\delta}$ were prepared by this method at a sintering temperature of 1050°C to form a perovskite phase.

(*ii*) *Preparation of Oxides by the Pechini Method*

$LaYO_3$ with the bixbyite structure and $La_{0.9}Sr_{0.1}O_{1.45}$ were prepared by the Pechini method (*14*). Nitrates of the required oxides were dissolved in distilled water and citric acid (2 moles per mole perovskite) was added to the solution. The solution was heated to 90°C and ethylene glycol was added while stirring. Further heating resulting in the evaporation of water followed by the emission of NO_x fumes and subsequent formation of a resin. The resin was charred at 450°C and crushed to yield a fine powder. For $LaYO_3$ the powder was sintered at 650°C for 12 hr to form a bixbyite phase of the nominal composition $LaYO_3$. For $La_{0.9}Sr_{0.1}O_{1.45}$, the powder was sintered at 800°C for 12 hr. This procedure ensures adequate mixing of cations when the final firing temperature is to be maintained below 800°C.

CHARACTERIZATION

(*i*) Identification of Phases

A Diano X-ray diffractometer was used to identify the phases which were present in the prepared oxides. A copper K_α radiation passed through a nickel filter was used as the source beam. All the samples used in this experiment were found to consist of the desired single phase within the limitations of the X-ray diffraction technique.

(*ii*) *Measurement of Surface Areas*

The surface areas of the prepared samples were measured by the single-point BET method using a Quantachrome Monosorb analyzer. Table 1 lists the prepared oxides and the surface area of each oxide.

(*iii*) *Catalytic Experiments*

Catalysts were tested in a fixed-bed quartz reactor (10 mm O.D) for the methane coupling reaction at a constant temperature of 795°C under steady-state conditions. This was selected to avoid complications arising from homogeneous gas-phase reactions. The apparatus has been described and calibrated elsewhere (*16*). The feed gas composition was 30% CH_4, 5% O_2, and 65% He. The total input feed rate was maintained constant at 100 cm^3/min. A catalyst weight of 0.4 g was used for the reaction in each case.

(*iv*) *Product Analysis*

The unreacted feed gases and the products were analyzed by an on-line gas chromatograph using a thermal conductivity de-

TABLE 1

List of Catalysts Examined for the Methane Coupling Reaction

Catalyst	Method of preparation	Sintering temp. (°C)	Structure	Conduction type	Surface area (m^2/gm)
$La_{0.8}Sr_{0.2}CrO_{3-\delta}$	Solid state	1100	Perovskite	p-Type	0.94
$La_{0.8}Sr_{0.2}MnO_{3-\delta}$	Solid state	1100	Perovskite	p-Type	1.36
$La_{0.8}Sr_{0.2}CoO_{3-\delta}$	Solid state	1100	Perovskite	p-Type	0.20
$LaFe_{0.8}Nb_{0.2}O_{3-\delta}$	Solid state	1100	Perovskite	n-Type	1.01
$La_{1.8}Sr_{0.2}CuO_{4-\delta}$	Solid state	950	K_2NiF_4	p-Type	0.80
$Nd_2CuO_{4-\delta}$	From (*15*)	—	Close to K_2NiF_4	n-Type	1.04
$Nd_{1.8}Ce_{0.2}CuO_{4-\delta}$	From (*15*)	—	Close to K_2NiF_4	n-Type	0.28
$LaYO_3$-bixbyite	Pechini	650	Bixbyite	Insulator	5.4
$LaYO_3$-perovskite	Solid state	1100	Perovskite	Insulator	1.08
$La_{0.8}Sr_{0.2}YO_{2.9}$	Solid state	1100	Perovskite	Electrolyte	1.1
$La_{0.9}Sr_{0.1}O_{1.45}$	Pechini	800	Hexagonal	—	1.44
La_2O_3	From manufacturer	—	Hexagonal	Insulator	2.4
Y_2O_3	From Y(NO3)3	800	Bixbyite	Insulator	6.4
SrO	From SrCO3	800	NaCl	Insulator	0.8

tector with Carbosphere and Haysep column packings. The outlet stream gases were analyzed for CO, CO_2, CH_4, C_2H_4, C_2H_6, and O_2. Any H_2O formed during the reaction was trapped before sampling the products and was not analyzed in this procedure.

The conversion of methane was calculated as the fraction of methane reacted according to

$$X = \left(1 - \frac{\text{moles CH}_4\text{ out}}{\text{moles CH}_4\text{ in}}\right). \tag{1}$$

The yields, ΣCO_x (sum of CO and CO_2) and ΣC_2 (sum of C_2H_4 and C_2H_6), were obtained as follows:

$$\Sigma CO_x = \frac{\text{moles CO + moles CO}_2}{\text{moles CH}_4\text{ reacted}}, \tag{2}$$

$$\Sigma C_2 = \frac{\text{moles C}_2\text{H}_4 + \text{moles C}_2\text{H}_6}{\text{moles CH}_4\text{ reacted}}. \tag{3}$$

RESULTS AND DISCUSSION

Table 1 lists the oxides used in this study along with their structures, conduction type, and processing parameters. Of all the compounds studied, only $LaYO_3$ has two crystal structures that can be achieved in a stable form at room temperature. The bixbyite structure of $LaYO_3$ as in Y_2O_3 is similar to the CaF_2 fluorite structure but with 25% of the oxygen sites being vacant. It is unlike the perovskite structure, since there is a large concentration of oxygen vacancies.

The perovskites with high p-type electronic conductivity did not yield any C_2 products. The only electronically conducting perovskites with C_2 yield were $La_{0.8}Sr_{0.2}MnO_{3-\delta}$ and $LaFe_{0.8}Nb_{0.2}O_{3-\delta}$, both of which are probably n-type under the conditions of the experiment. From Table 1, only those compositions with any significant C_2 yield are presented here. The concentrations of the different gases in the outlet stream and the percentage CH_4 converted are given in Table 2 for such compositions. The two perovskites with high electronic conduction show small C_2 yields and high CO_x yields, whereas the oxides in the La–Sr–Y–O system all show significant C_2 yields. $LaFe_{0.8}Nb_{0.2}O_{3-\delta}$ is believed to be an n-type conductor (*8*) under the reactor conditions of oxygen partial pressure. While $La_{0.8}Sr_{0.2}MnO_{3-\delta}$ is a p-type conductor in air, it is likely to be an n-type conductor under reducing conditions due to the stabil-

TABLE 2

Composition of Outlet Stream and Calculated Yields from Products

Catalyst	% CH_4 converted	Product (%)				Yield		
		CO	CO_2	C_2H_4	C_2H_6	ΣCO_x	ΣC_2	$C_2^=/C_2$
$La_{0.8}Sr_{0.2}MnO_{3-\delta}$	11.9	0.15	3.00	0.10	0.26	80.56	18.35	0.39
$LaFe_{0.8}Nb_{0.2}O_{3-\delta}$	11.4	0.21	2.74	0.08	0.26	80.57	18.88	0.32
$LaYO_3$-bixbyite	16.8	0.57	2.27	0.54	0.68	52.99	45.69	0.85
$LaYO_3$-perovskite	14.4	0.57	2.60	0.15	0.45	71.22	27.12	0.45
$La_{0.8}SrO_{0.2}YO_{2.9}$	15.4	0.35	2.44	0.42	0.68	55.50	43.70	0.61
$La_{0.9}Sr_{0.1}O_{1.45}$	18.3	0.28	2.06	0.75	1.05	38.79	59.59	0.72
La_2O_3	17.5	0.36	2.20	0.63	0.84	45.95	52.61	0.75
Y_2O_3	17.2	0.78	2.55	0.52	0.73	61.13	35.96	0.87

Note. Feed is 30% CH_4 + 5% O_2 + 65% He. Temperature = 795°C.

ity of Mn^{2+} ion. p-type conductors gave no C_2 yields, whereas n-type conductors exhibited small C_2 yields. The superconducting oxides were not found to be active for the coupling reaction.

The equilibrium composition for a feed gas containing 30% CH_4 + 5% O_2 + 65% He was calculated theoretically at 795°C. The results are displayed in Table 3. According to these results, the carbon activity in the solid state is equal to one, therefore there should be carbon deposition in solid form as coke. During our experiments, carbon deposition was occasionally observed on the catalysts. The theoretical equilibrium oxygen partial pressure for the feed composition calculated from the equilibrium concentrations of CO and CO_2 is 4×10^{-23} atm.

TABLE 3

Calculated Equilibrium Composition of Gas for 30% CH_4 + 5% O_2 + 65% He Input at 795°C

Species	Mole fraction in product (%)
CO(g)	6.938
CO_2(g)	0.075
CH_4(g)	0.902
C_2H_4(g)	1.50×10^{-5}
C_2H_6(g)	0.59×10^{-5}
C_3H_6(g)	2.52×10^{-9}
C_3H_8(g)	0.13×10^{-9}
H_2O(g)	0.423
H_2(g)	42.84
O_2(g)	3.24×10^{-21}
C (cryst. + liq.)	Activity = 1.00

In contrast, the concentrations of CO and CO_2 in the outlet stream show that the oxygen partial pressure is actually much higher than the theoretical equilibrium value. The experimentally observed oxygen partial pressure calculated from the outlet stream composition is a maximum of 1.37×10^{-16} atm for $La_{0.8}Sr_{0.2}MnO_{3-\delta}$ and a minimum of 3.65×10^{-18} atm for Y_2O_3. In all cases, the observed oxygen pressure is much higher than the theoretical oxygen partial pressure from thermodynamic calculations. The experimental oxygen partial pressure is still, however, quite reducing.

Among the compounds in the La–Y–O, strontium-substituted lanthanum yttrium oxide, $La_{0.8}Sr_{0.2}YO_{2.9}$, with the perovskite structure is an ionic conductor (*17*) with an ionic conductivity similar to that of the well known electrolyte, stabilized zirconia. The substitution of strontium for lanthanum in these compounds introduces oxygen vacancies in these materials. For a 20 mole% substitution of strontium for lanthanum, there are 3.33% oxygen vacancies introduced on the oxygen sublattice. Therefore both $La_{0.8}Sr_{0.2}YO_{2.9}$ and $La_{0.9}Sr_{0.1}O_{1.45}$ have a considerable anionic fraction of oxygen vacancies. Sr-substituted lanthanum oxides are also ionic conductors with conductivity

TABLE 4

Diffusion Coefficients of Selected Oxides

Composition	Temperature (°C)	Chemical diffusion coefficient (cm^2/s)
$La_{0.9}Sr_{0.1}CoO_{3-\delta}$ (*21*)	850	6.3×10^{-6}
$La_{0.9}Sr_{0.1}FeO_{3-\delta}$ (*21*)	900	7.41×10^{-6}
$La_{0.79}Sr_{0.2}MnO_{3-\delta}$ (*22*)	860	1.7×10^{-6}
$La_{0.8}Sr_{0.2}YO_{3-\delta}$	1000	1×10^{-5}
Y_2O_3 (*23*)	1000	2.63×10^{-9}

[a] Estimated from conductivity data of (*17*).

close to zirconia between 600 and 800°C (*18*).

The diffusion coefficient of oxygen in the electrolyte, $La_{0.8}Sr_{0.2}YO_{2.9}$, is greater than that of the manganite, $La_{0.79}Sr_{0.2}MnO_{3-\delta}$ (Table 4), which is consistent with the greater C_2 yield of the $La_{0.8}Sr_{0.2}YO_{2.9}$ solid solution if mobility of oxygen vacancies were important for coupling reactions. However, the diffusion coefficients of Y_2O_3 is considerably lower than that of $La_{0.79}Sr_{0.2}MnO_{3-\delta}$ and the other perovskites, while the C_2 yield is found to be much greater for Y_2O_3. The diffusion coefficient of oxygen, then, is not the only important factor for high C_2 yields.

For unsubstituted $LaYO_3$, it has been reported (*19*) that the bixbyite phase has a high C_2 yield whereas the perovskite phase has almost no C_2 yield for a feed gas containing 13.3% CH_4 + 6.65% O_2 + 80% He ($CH_4/O_2 = 2$) and also for $CH_4/O_2 = 5$ at 700°C. Our results indicate a significant C_2 yield for the perovskite as well as bixbyite phases both at 700 and 795°C. The strontium-substituted compound, $La_{0.8}Sr_{0.2}YO_{2.9}$, also is a perovskite with significant C_2 yield, as can be seen from Table 2. Therefore from our results, the basic crystal structure is only one important factor for C_2 yields, as was suggested by (*19*).

The substitution of strontium in $LaYO_3$ increases the concentration of oxygen vacancies in the electrolyte without making it an electronic conductor. A subsequent increase in C_2 yield is observed. In the other strontium-substituted perovskites, strontium addition not only increases the oxygen vacancies but also increases their electronic conductivity, and the C_2 yields are found to be smaller or negligible. Therefore a combination of an insulator or electrolyte combined with increased oxygen vacancy concentration appears to increase the C_2 yield. The $La_{0.8}Sr_{0.2}YO_{2.9}$ catalyst also exhibited the highest activity for total oxidation of methane among similar types of perovskite oxides (*20*).

CONCLUSIONS

A study of the coupling reactions on perovskite oxides, K_2NiF_4-type superconducting oxides, component oxides, and the solid solution $La_{0.9}Sr_{0.1}O_{1.45}$ has been performed. Materials with n-type conduction, electrolytes, and insulators resulted in the formation of C_2 products from CH_4. Among these, oxides from the La–Sr–Y–O system gave the highest C_2 yields. Within this system, oxides with a higher oxygen vacancy concentration, $La_{0.8}Sr_{0.2}YO_{2.9}$ and $La_{0.9}Sr_{0.1}O_{1.45}$, were found to be more active for coupling than the component oxides.

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